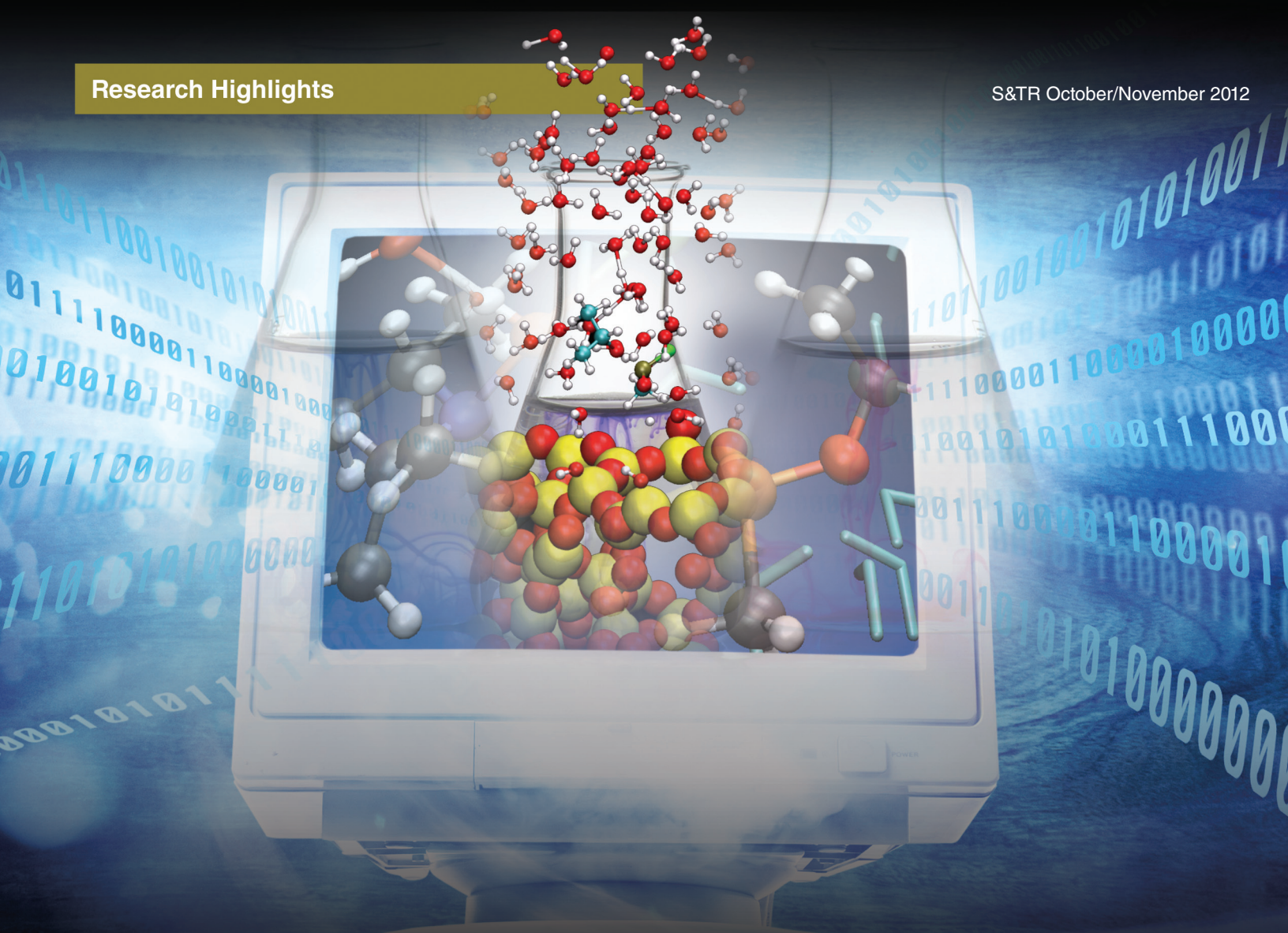


Breaking Down Nerve Agent Behavior

CHEMISTRY research immediately conjures imagery of scientists in lab coats mixing colorful reagents in flasks and beakers. It is becoming increasingly common, though, for traditional chemists to work side by side with computational chemists to probe the world at the atomic scale. Today's computational chemists are performing similar tasks to laboratory chemists, albeit in a virtual environment. As computing power increases and scientists are able to model the world around them with increasing fidelity, computational chemistry is emerging as an effective complementary approach to traditional laboratory experiments for better understanding of complex chemical behavior.

One area benefiting from these insights is the study of toxic substances such as nerve agents. Among the more dangerous components of humankind's destructive arsenal, nerve agents are potent chemical warfare agents that, if inhaled, swallowed, or absorbed through the skin or eyes, will inhibit the transmission of nerve impulses and swiftly cause death. In a post-9/11 world, with the lingering threat of terrorism, researchers have been working to supply national security personnel and emergency responders with reliable information on how best to remediate an area contaminated with a nerve agent, if such a dire situation were to occur. Restoration and remediation efforts will dramatically benefit from a molecular understanding of how nerve agents react chemically with potential decontaminants as well as adjacent surfaces. Computational chemistry offers an opportunity to study nerve agents without the risk incurred from handling these toxic chemicals.

Today, computer simulations allow researchers to perform fewer and more targeted laboratory experiments. Experimental chemist Bradley Hart, director of Livermore's Forensic Science Center (FSC), observes, "With laboratory experiments, it can be difficult to get at the mechanisms behind the chemical reactions. We see the reaction products and the reaction rates, but understanding the reaction process at an atomic level is more difficult. For example,

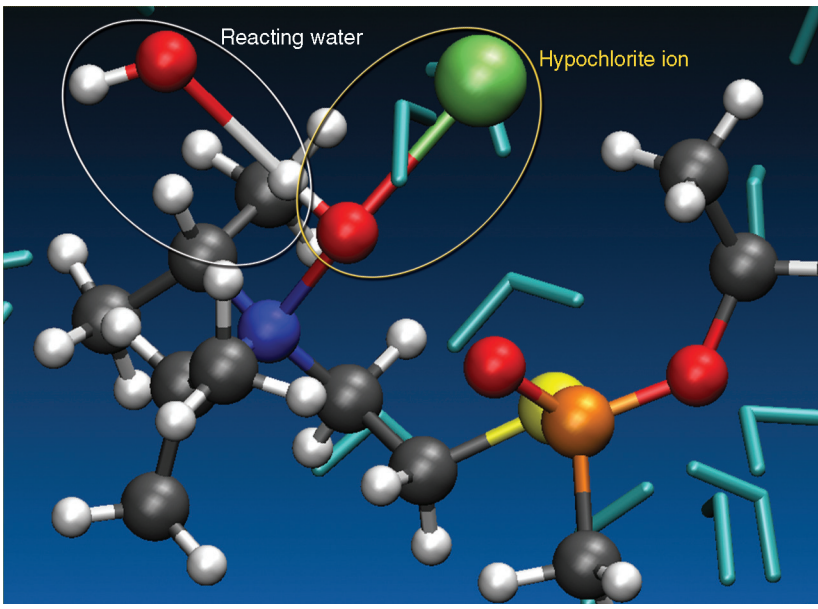
sometimes multiple reaction paths can lead to the same result." Computational chemistry is well suited for peering beneath the surface of reactions. Computational chemist Richard Gee says, "Experimentalists have to make many inferences, but computationalists can observe what's happening at an atomic level."

Saving Time

Gee and computational chemist William Kuo have led a successful effort to demonstrate a computational approach to decontamination research by characterizing how the nerve agents VX and sarin chemically degrade. Using the simulation suite CP2K on Livermore's 360-trillion floating-point operations per second (teraflops) BlueGene/L supercomputer, the researchers modeled the complex interactions between nerve agents and decontaminant molecules within a first-principles framework. Unlike most simulation techniques, first-principles simulations build models directly from quantum-mechanical principles and fundamental physical properties such as atomic mass and charge. This technique eliminates potential biases and assumptions about how atoms and molecules interact by calculating the forces dictating these reactions directly from a system's electronic structure and nature's basic laws. First-principles methods are ideal for modeling chemical processes where bonds can form, alter, or break. (See *S&TR*, October 2005, pp. 12–18.)

In a prototypical chemical reaction, a reactant is converted to a product at a rate determined by the activation energy barrier. With a low activation barrier, the chemical reaction can proceed quickly, while a high activation barrier impedes the reaction, causing it to proceed more slowly. Many chemical reactions can take microseconds to many seconds to occur, depending on the activation barrier involved. Unfortunately, even fast chemical reactions are computationally expensive to model with first-principles methods. Using BlueGene/L, it is only possible to directly simulate the interactions of hundreds of atoms for a span of picoseconds. Were researchers to run such a simulation, they would require an incredible stroke of luck to observe a chemical reaction of interest.

Bridging the temporal gap between chemical reaction and computer simulation necessitates improvements in simulation efficiency. By using a rare-event sampling method known as metadynamics to artificially accelerate the simulation time, the Livermore researchers were able to study many potential chemical degradation pathways. Metadynamics is a powerful and flexible algorithm for enhancing molecular-dynamics simulations and determining the free-energy surface—the multidimensional energy landscape of a reaction pathway—for a chemical reaction. For this technique, the researchers define a set of reaction possibilities to describe a multitude of potential reactions. Ideally, these variables examine a variety of potential reaction sites, including the surrounding medium.



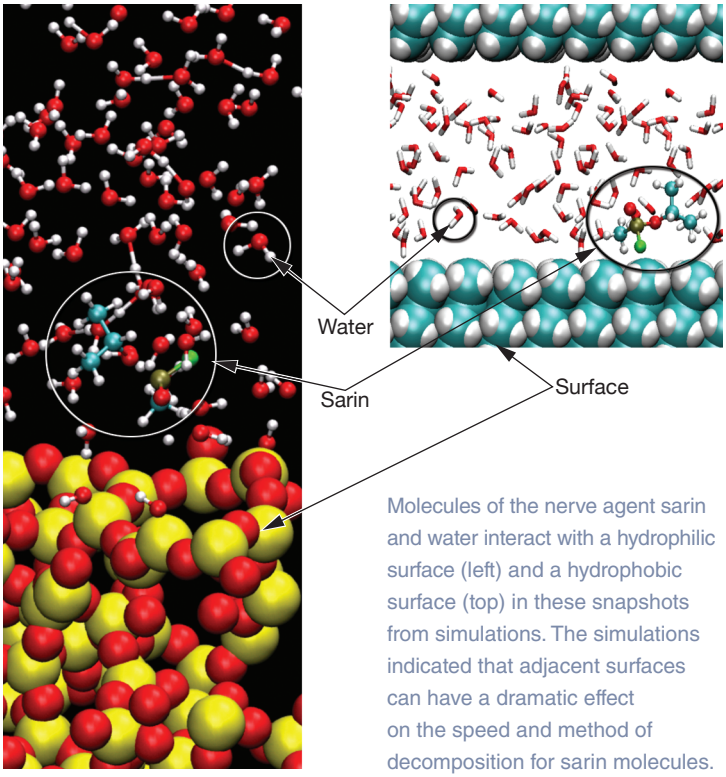
In this snapshot from a simulation of the nerve agent VX, an incoming hypochlorite ion (bleach) interacts with the nitrogen (blue) atomic center of VX. As the hypochlorite oxygen atom is displaced from the chlorine (green atom), the nitrogen also reacts with an adjacent water molecule. Water molecules not directly involved in the reaction are displayed as L-shaped objects. Computational chemists are using a metadynamics algorithm to efficiently examine potential reaction sites, such as VX's nitrogen atomic center.

A Close Match

Experiments have demonstrated that for the nerve agents VX and sarin, the most important chemical reactions are likely to occur at the phosphorus atomic center. It is here that the nerve agent molecule is most susceptible to a bond rupture, possibly resulting in a nontoxic product. The formation of the product can be accelerated by increasing temperature or adding a strong oxidizing agent, such as hypochlorite ions from bleaching powder. To provide a computational comparison, Gee and his team modeled VX behavior in the presence of bleach and water. Tracking the results in half-femtosecond intervals, they examined a variety of decontamination mechanisms and chemical-reaction energy barriers. They also examined how both the water and the bleach might affect the decontamination reactions, something that had not previously been studied computationally.

The degradation of nerve agents can occur through multiple reaction pathways. By leveraging computer resources and the metadynamics algorithm, the researchers could independently simulate each possible reaction pathway, not only at the phosphorus atomic center but also at the sulfur, nitrogen, and carbon atomic centers. Each potential pathway requires an independent simulation, which takes approximately 100,000 computing hours to execute.

VX had already been extensively studied in the laboratory, and the researchers found a solid match between the computed and



Molecules of the nerve agent sarin and water interact with a hydrophilic surface (left) and a hydrophobic surface (top) in these snapshots from simulations. The simulations indicated that adjacent surfaces can have a dramatic effect on the speed and method of decomposition for sarin molecules.

experimentally measured results. Gee says, "Our modeling results were surprisingly accurate and precise when compared with the experimental data." Kuo adds, "This modeling would not have been possible without fast computers and rare-event calculation methods."

In a related study, the researchers modeled the decontamination of sarin and compared their results to experiments conducted at FSC. Through reliable, efficient chemical modeling of the interactions between nerve agents, water, and bleach, Gee, Kuo, and their colleagues demonstrated the efficacy and precision of simulations for decontamination research.

Love–Hate Relationship

In a real remediation situation, nerve agents, water, and bleach interact within a complex chemical environment. Previous laboratory research has shown that sarin has only one path for decomposition in a standard liquid solution, but whether this holds true when sarin is adjacent to surfaces such as dirt, concrete, or linoleum has been unknown. Kuo notes, "Experiments have indicated that interfaces can have a profound effect on the chemistry for sarin, but it has been hard to pinpoint the effect." Different surfaces could potentially accelerate or retard decontamination. Building on their successful VX simulations, the researchers investigated potential degradation pathways for sarin in the presence of a hydrophilic (water-loving) or a hydrophobic (water-hating) surface.

For the hydrophilic surface, researchers modeled a slab of glass. The simulations revealed that when sarin was near the glass surface, the most probable decomposition mechanism was similar to that of a standard liquid solution, but the sarin broke down more quickly. The thin film of water in contact with the glass surface adopted a distinctive molecular arrangement, which likely helped lower the activation barrier by 30 percent. The hydrophobic surface, vinyl, produced the opposite effect. It not only raised the energy barrier by 20 percent but also changed the reaction path for molecular degradation.

These simulations involving extremely hydrophilic and hydrophobic surfaces effectively demonstrated the extent to which surfaces can influence sarin degradation. Gee is quick to note that the surfaces used in the simulations were idealistic, involving perfectly smooth crystals. "In the real world, at an atomic level, the topology of common materials is complex, containing many nonideal features," he says. "Such features may provide many places for a sarin molecule to hide from being chemically degraded." Still, the models are sufficiently realistic in that they provide a means to obtain useful information regarding how possible nerve agent degradation chemistry may change depending on the encountered surface. The simulations confirmed that surfaces within bonding distance of sarin could fundamentally affect its reaction rates and decomposition processes.

The ideal investigation of the chemical behavior of nerve agents should combine both modeling and experiments. As home to simulation experts, powerful computers, and scientists who can validate degradation mechanisms experimentally (see *S&TR,* May 2003, pp. 4–11; April 2002, pp. 11–18), Lawrence Livermore is uniquely qualified for such work. While this effort is still in its early stages, the research performed thus far supports using simulations to understand relevant reaction mechanisms. The results also indicate that computational chemistry could provide a viable means for screening decontamination formulations, with the goal of prioritizing promising substances and reducing the number of hazardous laboratory experiments required. Simulations examining the role of surfaces could also help guide Homeland Security and Defense Department personnel in customizing decontamination solutions to specific surfaces. Amassing reliable information on chemical weapon remediation methods enables a timely and effective response should a chemical attack ever come to pass.

—Rose Hansen

Key Words: BlueGene/L, computational chemistry, CP2K, energy barrier, first-principles simulation, metadynamics, nerve agent, rare-event sampling, sarin, transition state, VX.

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